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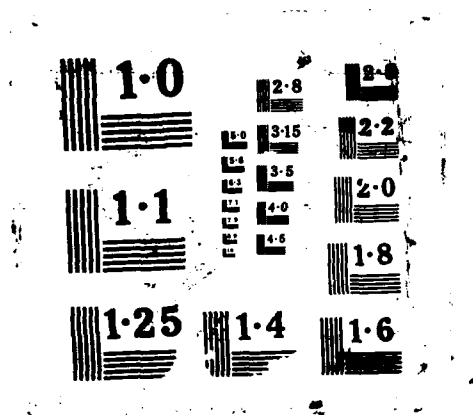
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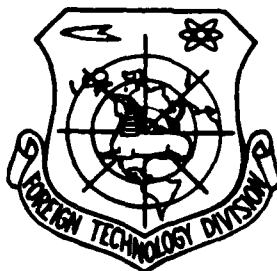
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HIGH-MOLECULAR COMPOUNDS
(Selected Articles)



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4 September 1987

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HIGH-MOLECULAR COMPOUNDS (Selected Articles)

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MT TRANSLATION CORRECTIONS

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Example:

Translation # FTD-ID(RS)T-0204-86 (Provided by SIT)

Foreign Page # _____

Incorrect word/phrase: _____

Recommendation: _____

Foreign page numbers occur in the English text and may be found anywhere along the left margin of the page as in this example:

In them occurs the state named "night blindness" - hemeralopia, which, according to the current point of view, is a result of damage of the rod-shaped apparatus of the eye.

Page 51.

However, in recent years it has been shown that with the hereditary pigment degenerations in animals the biochemical changes are observed in all cellular elements of the retina.

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U. S. BOARD ON GEOGRAPHIC NAMES transliteration SYSTEM

Block	Italic	Transliteration	Block	Italic	Transliteration
А а	<i>А а</i>	A, a	Р р	<i>Р р</i>	R, r
Б б	<i>Б б</i>	B, b	С с	<i>С с</i>	S, s
В в	<i>В в</i>	V, v	Т т	<i>Т т</i>	T, t
Г г	<i>Г г</i>	G, g	У у	<i>У у</i>	U, u
Д д	<i>Д д</i>	D, d	Ф ф	<i>Ф ф</i>	F, f
Е е	<i>Е е</i>	Ye, ye; E, e*	Х х	<i>Х х</i>	Kh, kh
Ж ж	<i>Ж ж</i>	Zh, zh	Ц ц	<i>Ц ц</i>	Ts, ts
З з	<i>З з</i>	Z, z	Ч ч	<i>Ч ч</i>	Ch, ch
И и	<i>И и</i>	I, i	Ш ш	<i>Ш ш</i>	Sh, sh
Й й	<i>Й й</i>	Y, y	Щ щ	<i>Щ щ</i>	Shch, shch
К к	<i>К к</i>	K, k	Ъ ъ	<i>Ъ ъ</i>	"
Л л	<i>Л л</i>	L, l	Ы ы	<i>Ы ы</i>	Y, y
М м	<i>М м</i>	M, m	Ь ь	<i>Ь ь</i>	'
Н н	<i>Н н</i>	N, n	Э э	<i>Э э</i>	E, e
О о	<i>О о</i>	O, o	Ю ю	<i>Ю ю</i>	Yu, yu
П п	<i>П п</i>	P, p	Я я	<i>Я я</i>	Ya, ya

*ye initially, after vowels, and after Ъ, Ь; e elsewhere.
When written as ѐ in Russian, transliterate as yě or ě.

RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English	Russian	English	Russian	English
sin	sin	sh	sinh	arc sh	\sinh^{-1}
cos	cos	ch	cosh	arc ch	\cosh^{-1}
tg	tan	th	tanh	arc th	\tanh^{-1}
ctg	cot	cth	coth	arc cth	\coth^{-1}
sec	sec	sch	sech	arc sch	sech^{-1}
cosec	csc	csch	csch	arc csch	csch^{-1}

Russian English

rot curl
lg log

GRAPHICS DISCLAIMER

All figures, graphics, tables, equations, etc.
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from the best quality copy available.

Page 565.

THE EFFECT OF SYNDIOTACTIC POLYMETHYL METHACRYLATE ON THE PROCESS OF ANIONIC POLYMERIZATION OF METHYLMETHACRYLATE.

L. K. Golova, Yu. B. Amerik, B. A. Krentsel'.

Dear editor

During the study of anionic polymerization of methymethacrylate (MMA) in solution of toluene on $p\text{-C}_4\text{H}_9\text{Li}$ in presence of syndiotactic polymethyl methacrylate (PMMA [- polymethyl methacrylate]) we discovered new stereochemical effects.

As is known, with anionic polymerization of MMA in solution of toluene is formed isotactic PMMA of following configuration composition: I=76, H=15, S=9% [9]. The additions of the preliminarily obtained isotactic samples of PMMA do not have an effect on the structure of newly forming isotactic PMMA under the same conditions of polymerization. On the contrary, the additive of syndiotactic PMMA (I=2.6, H=32.4, S=65%), capable of forming stereo-complex with isotactic PMMA [2], leads to a substantial change in the polymerization and structure of the generatrix of polymer.

With high concentrations of preliminarily obtained syndiotactic PMMA (>20%) in solution of MMA with anionic polymerization in

presence $p\text{-C}_6\text{H}_5\text{Li}$ atactic polymer is formed. With the concentrations of syndiotactic PMMA $< 10\%$ in the solution in the mixture of toluene and MMA is formed PMMA of stereo-block structure. For example, with the addition of 1 g of syndiotactic PMMA to the mixture of toluene (9 g) - MMA (1 g) in presence of $p\text{-C}_6\text{H}_5\text{Li}$ at 21° is formed PMMA of the following configuration composition: I - 34.5, H - 13.6, S - 51.5%. During the addition even of insignificant quantities of syndiotactic PMMA ($\text{MMA}:\text{PMMA} < 0.05$) the speed of anionic polymerization of MMA in entire interval of conversions exceeds the speed of anionic polymerization of MMA in the absence of PMMA.

Thus, in the case of adding syndiotactic polymer to reaction mixture of one of reasons, which have effect on structure of newly forming polymer, is capacity of isotactic and syndiotactic sections of chains to form stereo-complex [3].

Under conditions of forming stereo-complex, apparently, is possible selective solvation of counterions by sections of syndiotactic polymer chains with formation of free ions how is explained generation in active centers of syndiotactic (atactic) sections and increase in general/common speed of polymerization.

It was received by the editorial staff 12 Mar. 1970.

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Page 611.

SYNTHESIS AND OXIDATIVE DEHYDROPOLYCONDENSATION OF FORMALS OF TERTIARY ACETYLENE ALCOHOLS.

L. A. Akopyan, S. B. Gevorkyan, Ye. G. Kharatyan, S. G. Matsoyan.

Earlier was shown [1], that diacetylene compounds with terminal tertiary acetylene groups in contrast to dipropargylic derivatives during oxidative combination form exceptionally/exclusively soluble fusible polymers, whose basic part consists of cyclic oligomers. Was made the assumption that the insolubility of the polymers, obtained from the diacetylenes with the terminal primary acetylene (propargylic) groups, was caused by side oxidative reaction due to the active hydrogen, which is found in α -position to triple bond [1]. It was interesting to study oxidative combination of α , ω -diacetylenes with the tertiary acetylene groups based on the example of the new class of compounds.

This work is dedicated to synthesis and oxidative dehydropoly-condensation of formalis of series/number of tertiary acetylene alcohols: dimethyl-, methylethyl-, methyl-tert.butylethynylcarbinols and 1-ethynylcyclohexanol.

It was established that tertiary acetylene alcohols during

boiling in solution in benzene with paraform in presence of p-toluenesulfonic acid form appropriate formals with output/yield 30-50%:



Table 1 gives output/yield and properties of synthesized formals of tertiary acetylene alcohols, used for obtaining polymers by method of oxidative combination. For the comparison of the properties of polymers was synthesized also acetal with the primary acetylene group - formal of propargylalcohol.

Oxidative dehydropolycondensation was conducted in pyridine in presence of copper monochloride at 30°. Oxygen served as oxidizer.

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Table 1. Formals of tertiary acetylene alcohols

Исходный мономер, № (1)	R	R'	Выход, % (2)	Т. кип. °С./мм. (3)	Брутто- формула (4)	n _D ²⁰	d ₄ ²⁰	MRD		(5) Анализ, %			
								найдено (6)	вычислено (7)	C		H	
										найдено (8)	вычислено (9)	найдено (10)	вычислено (11)
1	H	H	68.5	63/12	C ₁₁ H ₁₄ O ₂	1.4450	—	—	—	—	—	—	—
2	CH ₃	CH ₃	44.4	66-67/10	C ₁₁ H ₁₆ O ₂	1.4325	0.8908	52.53	52.28	72.98	73.30	9.14	8.94
3	CH ₃	C ₂ H ₅	43.2	96/11	C ₁₂ H ₁₈ O ₂	1.4455	0.9002	61.65	61.51	74.80	74.96	9.53	9.68
4	CH ₃	C(CH ₃) ₂	37.8	89/2	C ₁₁ H ₁₆ O ₂	1.4540	0.8994	79.61	79.98	77.20	77.22	10.96	10.67
5	R + R' = —	(CH ₃) ₂ —	37.6	110/1	C ₁₁ H ₁₆ O ₂	1.4931	1.0031	75.45	75.58	78.18	78.42	9.49	9.29

Key: (1). Initial monomer. (2). Output/yield. (3). Boiling point. (4). Sum formula. (5). Analysis. (6). found. (7). calculated.

FOOTNOTE ¹. According to data [2] n_D²⁰ 1.4430. ENDFOOTNOTE.

Table 2. Some properties of synthesized polymers.

Полимер № 1 (1)	Выход полимера, % (2)	Внешний вид полимера (3)	[η] в бензоле (4)	T _g	M _n		(5) Анализ, %			
					абсолютно- численно (6)	по конечным группам (7)	C		H	
							найдено (8)	вычислено (9)	найдено (10)	вычислено (11)
1	89.5	Красный порошкообразный ⁽¹²⁾	—	—	—	—	60.97	68.85	4.83	4.95
2	79.3	Коричневый 2- каучуко- подобный ⁽¹¹⁾	0.42	—	—	—	74.10	74.13	8.02	7.92
3	53.6	Оранжевый 2- каучуко- подобный ⁽¹²⁾	0.39	—	—	—	79.91	75.70	8.75	8.80
4	86.9	Белый порошкообразный ⁽¹⁵⁾	0.12	80	5200	24 200	78.00	77.82	9.84	9.99
5	90.8	Желтый порошкообразный ⁽¹⁴⁾	0.21	73	8400	35 200	79.00	79.03	8.30	8.58

Key: (1). Polymer, No. ¹.

FOOTNOTE ¹. The numbers of polymers correspond to the numbers of initial monomers in Table 1. ENDFOOTNOTE.

(2). Output/yield of polymer. (3). Appearance of polymer. (4). in benzene. (5). Analysis. (6). ebullioscopically. (7). on end groups. (8). found. (9). calculated. (10). Red powder-like. (11). Brown ² rubberlike.

FOOTNOTE ². Before drying out polymers were white color.

ENDFOOTNOTE.

(12). Orange ² rubberlike. (13). White powder-like. (14). Yellow powder-like.

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Conducting polycondensation in the solution in the pyridine has the advantage that the solvent, being the simultaneously complexing component, equally dissolves well both the monomers and products of their polycondensation. The obtained polymers were thoroughly purified by repeated settling from the solutions in the acid, alkaline and neutral media; the absence of copper in the polymers was controlled by analysis. Special experiments established that the obtained poly-formals under the conditions for cleaning/decontamination (processing/treatment in the acid medium) do not undergo noticeable hydrolysis.

As one would expect, formals of tertiary acetylene alcohols form soluble fusible polymers, whereas oxidative combination of formal of propargylalcohol leads to formation of nonmelting, undissolved polymer

[3]. It is interesting to note that the latter in the absence of residual copper showed disagreement in the obtained and calculated values of carbon content, which confirms the validity of assumption about the side oxidative reaction due to hydrogen of methine group.

Table 2 gives output/yield and some physicochemical characteristics of synthesized polymers. As can be seen from this table, molecular weights of the polymers of formals of methyl-tert.butylethynylcarbinol and 1-ethynylcyclohexanol, determined ebullioscopically and by the end groups, do not coincide, moreover in the second case the overstated results are obtained. This disagreement we have noticed also on the polymers α , γ -di-(dimethylethynylmethyl) ester/ether of glycerin and its acetate and is explained by the possible cyclization of the linear macromolecules.

Experimental part.

Synthesis of formals of acetylene alcohols. In the flask/bulb, equipped with water separator of Dean-Stark and reflux condenser placed 0.2 moles of acetylene alcohol, 50 ml of benzene, 3 g of paraform and 0.5 g of p-toluenesulfonic acid. They boiled reaction mixture for 1 hour, cooled to room temperature, treated by potash, filtered and precipitate was washed in dry benzene. Solutions were united, benzene they distilled in the vacuum, and remainder/residue was subjected to fractional distillation.

Table 1 gives output/yield and some physicochemical constants of synthesized formals.

Oxidative dehydropolycondensation of formals of acetylene alcohols. In the three-necked flask/bulb, equipped with the mechanical agitator, reflux condenser and bubbler, were placed 0.3 g of copper monochloride and 30 ml of dry pyridine. Mixture was mixed before the complete dissolution of catalyst and were added 0.015 moles of formal of acetylene alcohol. During the intensive mixing through the reaction mixture at 30° during 6 hours they drew current of dry oxygen with a velocity of 45 cm³/min. Polymer was thoroughly purified by settling consecutively/serially from the solution in the pyridine by water, twice of dioxane ($R = CH_3$, $R' = CH_3$, C_2H_5) and ethylacetate ($R = CH_3$, $R' = C(CH_3)_3$, $R + R' = -(CH_2)_3$) by the diluted (1:10) hydrochloric acid, of the same solutions - 2% KOH and latter/last time by water.

Undissolved polymer of formal of propargylalcohol was separated/liberated, pouring out reaction mixture into water, they twice treated by boiling diluted hydrochloric acid (1:10), they thoroughly washed in water. Polymers were dried in the vacuum 12 mm at 76° (Table 2).

Determination of molecular weight of polymers. The measurement of numerical average molecular weight was conducted in the ebullioscope of the construction/design of yard in the benzene. For

the guarantee of the accuracy of measurements to the ebullioscope was adapted the water separator of Dean-Stark, that ensures the self-purification of solution from the water.

Determination of molecular weight from terminal acetylene groups was conducted by graphic method. For graphing of the dependence between the concentration of acetylene groups and the integrated intensity of the IR-spectrum of absorption (strip 3310 cm^{-1}) as the models the appropriate monomers were used.

Determination of temperature of vitrification (T_g) of polymers. Determination T_g of the obtained polymers was conducted in the instrument, designed by Tsetlin et al. [4]. The thermomechanical curves of polymers are taken with the load 0.34 kgf/cm^2 and increase in the temperature at a rate of $75\text{--}80\text{ deg/h}$. T_g was determined by the extrapolating of the straight portion of thermomechanical curves to the axis of abscissas.

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Conclusions/derivations.

1. Not recorded formals of series/number of tertiary acetylene alcohols are synthesized and their oxidative dehydropolycondensation is carried out.

2. It is shown that in contrast to dipropargylic derivatives

oxidative combination of diacetylene compounds with terminal tertiary acetylene groups leads to soluble fusible of polymer.

Institute of organic chemistry of AS of ArmSSR.

It was received by the editorial staff 7 JULY 1969.

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